

# Kinetic modeling of the electrochemical removal of ammonium and COD from landfill leachates

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**Abstract** Leachates generated from municipal landfills are complex effluents that contain high concentrations of organic pollutants, ammonium, chloride and many other soluble compounds. The aim of this study is to develop a generalized mathematical model for the description of the kinetics of the electro-oxidation of COD and  $\text{NH}_4^+$  contained in landfill leachates at boron doped diamond anodes. This complex scenario has been structured by defining two regimes for COD oxidation kinetics: (i) for  $j_{\text{lim,COD}} < j_{\text{appl}} \leq (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$  only direct and  $\bullet\text{OH}$  mediated oxidation reactions close to the anode surface occur, and the process is mass transfer controlled and described by the mass transfer coefficient  $k_m$ , a parameter affected by the hydrodynamics of the cell; ii) for  $j_{\text{appl}} > (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$  indirect oxidation in the bulk takes place which is quantified by an adjustable parameter  $k$ , for which a correlation with the applied current and the chloride concentration has been obtained. Ammonium oxidation occurred by electrogenerated chlorine, for which a second adjustable parameter  $k'$  has been defined.  $k'$  has been correlated to the initial COD concentration and the applied current, expressed as  $(A/V) \cdot (j_{\text{appl}}/j_{\text{lim,COD}})$ . The robustness of this model was corroborated by its good description of the experimental results obtained with leachates from two landfill sites located at Chania (Greece) and Meruelo (Spain), and with variable degrees of

pretreatment, therefore with a wide range of compositions, and for different operating conditions. The model developed from laboratory scale data was validated at pilot scale with a total BDD anodic area of  $1.05 \text{ m}^2$ .

**Keywords** Landfill leachates · BDD anodes · Ammonium oxidation · COD oxidation · Mathematical modeling of electro-oxidation

## 1 Introduction

Several mathematical models that describe the processes occurring in the anodic oxidation of organic compounds by means of boron doped diamond (BDD) electrodes have been developed [1]. The first model to describe the electrochemical oxidation of organic pollutants was proposed by Comninellis' group [2, 3] and it only considered direct and/or hydroxyl radical mediated oxidation of organic contaminants. This model is usually able to predict the behavior of the system as long as indirect oxidation processes do not take place. Cañizares et al. [4] proposed a model in which the electrochemical reactor was represented by a combination of three interconnected stirred tank reactors: two of these reactors represented the cathodic and anodic reaction zones with a volume equal to that of the diffusion layers for the direct or hydroxyl mediated reactions, while the third reactor represented the bulk zone, where the indirect oxidation chemical reactions take place. Mascia et al. [5] described the oxidation of organic compounds by means of hydroxyl radicals at BDD anodes. Changes with spatial position in the diffusion layer were taken into account. Thus in the diffusion layer, diffusion of organics and their reaction with hydroxyl radicals were considered. The latter reaction was described by second-order kinetics, i.e., first order with respect to the

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concentration of hydroxyl radicals and first order with respect to the concentration of organics. The bulk was represented by a stirred tank reactor. Recently, Mascia et al. [6] have gone a step further and have modified this model so that it can describe the oxidation of organics not only by means of hydroxyl radicals near the anode surface but also by means of electrogenerated active chlorine in the bulk. However, although these models reproduced the experimental data obtained during the electrochemical oxidation of synthetic wastewaters contaminated with a wide variety of organic pollutants with great precision, they still have to be validated for real wastewaters with complex and unknown detailed composition.

The treatment of landfill leachates using BDD anodes has been studied in our preceding works with raw and diluted leachates, analyzing the influence of the applied current and initial concentrations of organic contaminants [7, 8]. The excellent removal efficiency led to the on-site investigation using a pilot plant with a BDD anode area of 1.05 m<sup>2</sup> that was tested for biologically pretreated leachates [9] and also as a polishing step after Fenton treatment of the raw leachates [10]. The formation of oxidation by-products such as nitrate ions [11] as well as chlorinated compounds was a matter of concern when considering the electrochemical treatment of landfill leachates [12]. In this context, deployment of electrochemical oxidation in combination with ion exchange or reverse osmosis [13] has been proposed.

The aim of this study is to develop a generalized mathematical model for the description of the kinetics of the electro-oxidation at BDD anodes of NH<sub>4</sub><sup>+</sup> and organic pollutants, the latter expressed as Chemical Oxygen Demand (COD), contained in landfill leachates. The use of BDD anodes promotes the generation of hydroxyl radicals, while the high content of chlorine induces the simultaneous formation of free chlorine. At the usual range of Cl<sup>−</sup> concentration contained in the leachates, COD is oxidized primarily. Chlorine evolution is enhanced at lower COD concentrations, then causing indirect oxidation of ammonium. Nevertheless, an excess of free chlorine also contributes to the indirect oxidation of COD. The robustness of the model is corroborated by its application to leachates generated in two different landfill sites, with diverse pretreatment degrees and thus significant differences in the initial concentration of the main components, and for different operating conditions. Finally, the model is validated with data obtained at larger scale in a pilot plant operated on-site.

## 2 Experimental background

The leachate samples used in the experimental study were withdrawn from two intermunicipal sanitary landfill sites,

located in the prefecture of Chania (W. Crete, Greece), and in the municipality of Meruelo (Cantabria, Northern Spain). Table 1 shows that only marginal differences between the physico-chemical properties of the raw leachates from both landfill sites seem to exist. It is worth noticing that all wastewaters have a high electrical conductivity value permitting the application of electrochemical oxidation without the addition of extra electrolytes. In a previous study [10], the biologically treated leachate was further exposed to a Fenton treatment to oxidize the residual refractory organic matter, although it was found that the concentration of ammonium remained practically unaltered [14]. For this reason, electrochemical oxidation was tested as a polishing step in the removal of residual COD and ammonium. Kinetic data of COD and ammonium evolution with the electro-oxidation time were obtained at laboratory scale in two experimental systems, details given elsewhere [7, 12]. In both systems, single compartment electrolytic flow-cells that incorporate BDD anodes were used, with an anode area of 0.007 m<sup>2</sup> each one. Large scale tests were conducted in a pilot plant with a total anodic area of 1.05 m<sup>2</sup>, described in a previous work [15].

## 3 Results and mathematical modeling

Electrochemical oxidation of landfill leachates is significantly dependent on two process variables: i) the applied current density ( $j$ ) and ii) the composition of the aqueous waste. It needs to be reminded that landfill leachates are complex mixtures of organic compounds, ammonium, and dissolved salts at variable concentrations. The effect of the initial concentrations of COD and ammonium on the oxidation kinetics of both compounds, using BDD anodes was studied [7] using the raw leachate obtained from the landfill site of Meruelo (Spain), while additional samples obtained by dilution were compared. The chloride concentration was maintained approximately constant by the addition of NaCl to the diluted batch. It was observed that ammonium oxidation occurs at a slower rate than COD oxidation. Faster removals were obtained at lower initial concentrations of both pollutants. Interestingly, the effect of the initial contaminant load was more pronounced on ammonium than on COD removal. This behavior can be explained by the role of chloride ions present in the leachate that may react on BDD to give dissolved chlorine. The latter species hydrolyses in water to form hypochlorous acid and hypochlorite. Finally, hypochlorous acid rapidly reacts with ammonium [8]. Then, it happens that by lowering down the initial COD concentration while maintaining the initial concentrations of chloride ions constant, chloride evolution is enhanced which in turn results in higher ammonium oxidation rates.

**Table 1** Physico-chemical properties of the landfill leachates used in this study

Parameter	Landfill site of Chania (Greece) Raw leachate	Landfill site of Meruelo (Spain)		
		Raw leachate	Effluent from biological treatment	Effluent from Fenton treatment
pH	8.4	8.4	7.5–9	8.5
Conductivity (mS/cm)	22.6	12.8	9.1–14.4	9.4
TOC (mg/L)	n.a.	2,780	432–1,300	150–303
COD (mgO <sub>2</sub> /L)	3,385	4,430	1,130–1,750	350–747
BOD <sub>5</sub> (mg/L)	500	1,196	120	n.a.
BOD <sub>5</sub> /COD	0.15	0.27	0.11	n.a.
[NH <sub>4</sub> <sup>+</sup> ] (mg/L)	1,500	2,343	708–1,042	637–1,075
Chloride (mg/L)	2,587	3,230	1,560–2,166	975–1,612
Nitrite (mg/L)	<2	n.d.	n.d.–20	n.d.
Nitrate (mg/L)	1.9	n.d.	n.d.–700	100–790
Sulfate (mg/L)	11	39	172	2,643–7,325

Average values in the case of raw leachates and range of variation for treated leachates  
*n.a.* not available, *n.d.* not detected

Regarding the effect of current density, the rate of COD and ammonium oxidation increases with current density [9], as it was exemplified using leachates obtained from the landfill site located at Meruelo (Spain) that had been biologically pretreated which resulted in lowering down the initial concentration of the contaminants (see Table 1). This suggests that, at higher current densities, indirect oxidation by means of chlorine-mediated reactions plays an important role in the overall electrochemical oxidation of organics. The ammonium concentration profiles presented an initial delay that is consistent with an oxidation mechanism in which oxidation of organics takes place predominantly during the initial stage of the process. As the concentration of COD decreases, chlorine evolution, which initially takes place at a slow rate, gains importance and then electrochemically generated free chlorine oxidizes ammonium. A similar effect was observed when dealing with the leachates of the landfill site of Chania (Greece) [12], although in the latter case a larger volume of leachate sample was electrooxidized using the same anodic area as in the experiments performed in Spain, and thus longer treatment times were required to attain equivalent COD and ammonium removal percentages. Finally, experimental data obtained at pilot plant scale and varying the ratio of treated volume over anodic area were also gathered [15].

The above results demonstrated that electro-oxidation of landfill leachates follows a similar pattern independently of the origin of the leachate and of whether it has been previously pretreated or not. Current density and initial concentration of ammonium and COD have been found [7] to be the most important variables regarding the electro-oxidation of COD and ammonium. Higher current densities and lower COD and ammonium concentrations resulted in higher oxidation rates of these pollutants. The analysis showed [9] that a strong correlation between these

variables exists. These considerations are taken into account to develop a mathematical model that is able to describe ammonium and COD oxidation kinetics during electrochemical oxidation of landfill leachates.

### 3.1 COD oxidation kinetics

The model developed for COD oxidation is a modification of the model proposed by Comninellis [2]. In Comninellis' model, the main assumptions are that direct and/or indirect oxidation by means of hydroxyl radicals is thought to be responsible for the oxidation of the organic compounds. The reaction between  $\bullet\text{OH}$  and organics is considered to be a fast reaction and is controlled by the mass transport of the organics to the electrode surface. Also, oxidation of organics in the bulk with electrogenerated oxidants is thought to be negligible.

However, in the electrochemical treatment of landfill leachates, indirect oxidation of both organics and ammonium by means of electrogenerated active chlorine seems to have a relevant role. As it has been shown in the above presented results, in the three components “organic compounds/NH<sub>4</sub><sup>+</sup>/Cl<sup>−</sup>” mixtures found in the leachate, electrogenerated active chlorine reacts with ammonium primarily. As a result the chlorine evolution reaction becomes a parasitic reaction as far as COD is concerned because it consumes current that would have otherwise been destined to the oxidation of organic matter. Nonetheless, the results obtained with landfill leachate lead to the conclusion that if there is an excess of active chlorine in the solution (i.e., the concentration of active chlorine is higher than that necessary to oxidize ammonium), then active chlorine also participates in the oxidation of COD. Based on these assumptions and observations, the following operating regimes can be defined for the oxidation of

landfill leachates using BDD anodes as a function of the applied current density  $j_{\text{appl}}$ :

$$(i) \quad j_{\text{lim,COD}} < j_{\text{appl}} \leq (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$$

The oxidation of COD is governed by the mass transport of organic compounds to the electrode surface. Active mediated oxidation mechanisms do not participate in the oxidation of COD since electrogenerated chlorine is consumed by ammonium. The kinetics of COD oxidation in a batch system is described by Eq. 1,

$$\text{COD}(t) = \text{COD}_0 \exp[-(Ak_m/V)t] \quad (1)$$

where  $k_m$  is the mass transport coefficient,  $A$  is the electrode area, and  $V$  is the volume of the feed leachate. The limiting current density  $j_{\text{lim}}$  for organics mineralization is calculated as  $j_{\text{lim,COD}} = 4Fk_m\text{COD}_0$  [16], while the limiting current density for ammonium oxidation is calculated as  $j_{\text{lim,NH}_4^+} = 3Fk_m[\text{NH}_4^+]_0$  [7], where  $F$  is the Faraday's constant.

$$(ii) \quad (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+}) < j_{\text{appl}}$$

Oxidation of COD takes place by means of hydroxyl radicals and of electrogenerated oxidants. It should be underlined that besides active chlorine, other oxidants such as hydrogen peroxide and peroxodisulfate could be responsible for the higher oxidation rate. Usually, the kinetics of the oxidation reactions between organic compounds and oxidants ( $\text{HClO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ) is considered to be second order: i.e., first order with respect to the concentration of the electrogenerated oxidants ( $[\text{Ox}]$ ) and first order with respect to the concentration of the organic compounds  $[\text{COD}]$  (Eq. 2). Nonetheless, if the concentration of the electrogenerated inorganic oxidant is high, it can be considered to be independent of time, and it can be approximated to pseudo-first-order kinetics (Eq. 3)

$$r = -k_{\text{ox}} \cdot [\text{Ox}] \cdot [\text{COD}] \quad (2)$$

$$r = -k \cdot [\text{COD}] \quad (3)$$

In Eqs. 2 and 3,  $k_{\text{ox}}$  and  $k$  are the apparent second-order and pseudo-first-order kinetic constants, respectively. The latter will depend on the same variables that the concentration of inorganic oxidants does, such as current density.

Consequently, for  $j_{\text{appl}} > (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$ , the mass balance for COD is represented by the following equation,

$$V \frac{d[\text{COD}]}{dt} = -A \cdot k_m \cdot \text{COD} - k \cdot V \cdot \text{COD} \quad (4)$$

which combines the oxidation of COD by direct  $\bullet\text{OH}$  mediated oxidation near the anode surface, with the oxidation in the bulk by active chlorine. The integration of Eq. 4 gives,

$$\text{COD}(t) = \text{COD}_0 \exp[-(Ak_m/V + k)t] \quad (5)$$

### 3.2 Ammonium oxidation kinetics

At the landfill leachate's inherent pH value ( $\approx 8.4$ ), ammonium is primarily oxidized via a chlorine-mediated pathway. Ammonium oxidation kinetics in the presence of organic compounds shows sigmoidal ammonium concentration profiles [7]. Then the kinetics of chlorine reaction with ammonium is second order, i.e., first order in the free active chlorine concentration and first order in the concentration of ammonium

$$\frac{d[\text{NH}_4^+]}{dt} = -k_{\text{app}}[\text{NH}_4^+][\text{Cl}_2] \quad (6)$$

where  $k_{\text{app}}$  is the apparent second-order rate constant and  $[\text{Cl}_2]$  is the concentration of dissolved active chlorine ( $\text{HClO}$  +  $\text{ClO}^-$ ). Thus, if the kinetics of oxidation (Eq. 6) together with the discharge of chloride ions (Eq. 7) controls the overall oxidation rate, ammonium concentration profiles should follow a second-order kinetic trend. Equation 7 describes the evolution of chlorine concentration with electrolysis time. It considers that the rate of chlorine loss reactions due to the reduction of active chlorine at the cathode, to the anodic oxidation to  $\text{ClO}_3^-$  and to the homogeneous reaction with  $\text{NH}_4^+$  are much lower than the chlorine production rate,

$$\frac{d[\text{Cl}_2]}{dt} = \frac{\phi j A}{n F V} \quad (7)$$

where  $\phi$  is the current efficiency for chlorine evolution. The substitution of the integrated form of Eq. 7 in Eq. 6 gives,

$$\ln \frac{[\text{NH}_4^+]}{[\text{NH}_4^+]_0} = -k_{\text{app}} \frac{\phi j A}{n F V} = -k' t^2 \quad (8)$$

In order to use the proposed models, the values of three parameters are needed: i.e., the mass transfer coefficient  $k_m$  related to the mass transport rate of organic compounds from the bulk to the electrode surface, and the indirect oxidation kinetic constants of Eqs. 5 and 8,  $k$  and  $k'$ , related to the chlorine-mediated oxidation of organic compounds and ammonium.

### 3.3 Parameter $k_m$

The dependence of the mass transfer coefficient  $k_m$  on the hydrodynamic conditions has been described in a previous work [15] as follows,

$$Sh = a Re^{0.385} Sc^{0.20} \quad (9)$$

where  $Sh$ ,  $Re$ , and  $Sc$  stand for the Sherwood, Reynolds, and Schmidt numbers, respectively. When modeling kinetic results, it was found that the value of the

**Table 2** Operating conditions of the experiments used for the estimation of the model parameters  $k$  and  $k'$ , and validation of the model at pilot plant scale

Scale	Exp	Type of leachate	$V$ (L)	$A$ (m <sup>2</sup> )	$J$ (A m <sup>-2</sup> )	COD <sub>0</sub> (mg L <sup>-1</sup> )	[NH <sub>4</sub> <sup>+</sup> ] <sub>0</sub> (mg L <sup>-1</sup> )	[Cl <sup>-</sup> ] <sub>0</sub> (mg L <sup>-1</sup> )	$k \cdot 10^5$ (s <sup>-1</sup> )	$k'$ (h <sup>-2</sup> )
Laboratory	1	Raw leachate	10	0.007	1,200	3,142	1,380	2,587	–	0.0036
	2	Chania (Greece)			1,714	3,177	1,380	2,587	1.23	0.0044
	3				2,571	3,344	1,380	2,587	1.23	0.0065
	4	Raw leachate	1	0.007	900	3,799	2,076	2,760	7.19	0.060
	5	Original and diluted			600	3,275	2,453	3,030	2.97	0.018
	6	Meruelo (Spain)			600	1,728	1,348	2,160	6.62	0.103
	7				300	1,813	1,145	2,060	3.02	0.016
	8				300	853	591	1,790	6.46	0.087
	9				150	773	591	1,900	1.91	0.019
	10	Biologically pretreated leachate	1	0.007	300	1,497	933	2,127	1.25	0.030
	11	Meruelo (Spain)			450	1,448	980	1,820	5.82	0.094
	12				600	1,398	980	2,941	9.75	0.143
	13				900	1,349	910	2,020	18.8	0.241
	14				1,200	1,430	980	2,127	24.6	0.355
Pilot plant	15	Biological + Fenton pretreatments	1	0.007	100	368	857	1,543	1.25	0.025
	16	Meruelo (Spain)			300	306	871	1,612	9.49	0.132
	17				450	316	657	975	21.4	0.221
	18	Biologically pretreated leachate	250	0.35	450	960	905	1,700	Calculated from Eq. 10	Calculated from Eqs. 11, 12
	19	Meruelo (Spain)	500	1.05	450	681	906	1,617		
	20		250	1.05	300	941	912	1,546		
	21		250	1.05	450	960	905	1,700		
	22		250	1.05	600	851	828	1,531		
	23		250	1.05	900	770	630	1,523		
	24		250	1.05	1,200	770	639	1,471		

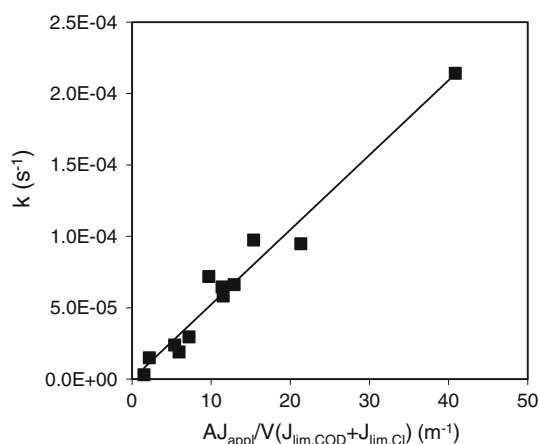
pre-exponential parameter  $a$  depends on the value of the interelectrode gap ( $S$ ). The three cells used in the experimental work were always formed by two circular parallel plates; however, the interelectrode gap varied as follows: case (1) cell used at laboratory scale in Greece,  $S = 10$  mm; case (2) cell used at laboratory scale in Spain,  $S = 5$  mm, and case (3) cell used at pilot plant scale in Spain,  $S = 1$  mm. The limiting current technique [17], employing the oxidation of ferrocyanide ion to ferricyanide ion as model reaction, was used to determine the values of the mass transfer coefficient  $k_{m,i}$  for each of the three cells under the applied flow rates used in the experiments:  $k_{m,1} = 1.75 \times 10^{-5} \text{ m s}^{-1}$  [18],  $k_{m,2} = 1.2 \times 10^{-5} \text{ m s}^{-1}$  ( $Q_2 = 11 \text{ L min}^{-1}$ ),  $k_{m,3} = 1.6 \times 10^{-5} \text{ m s}^{-1}$  ( $Q_3 = 6 \text{ L min}^{-1}$ ). Then these values were used in Eq. 9 to determine the parameter  $a$  values in each case [15], equal to  $a_1 = 2.45$ ,  $a_2 = 1.67$  and  $a_3 = 0.54$ .

### 3.4 Parameter $k$

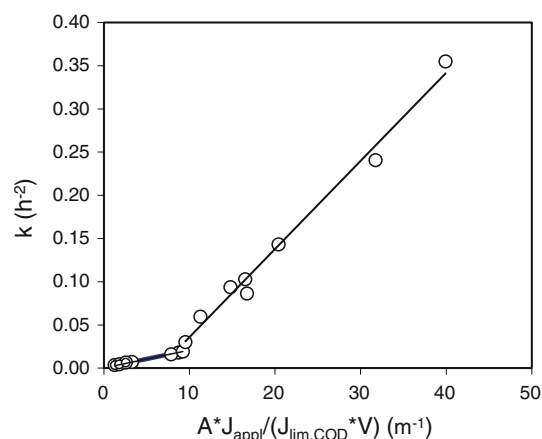
The value of the parameter  $k$  was determined by fitting the experimental data [7, 9, 10, 12, 15] to Eq. 5. The estimated values of  $k$  are given in Table 2. In Fig. 1 it can be observed that the value of  $k$  ( $\text{s}^{-1}$ ) increases linearly with  $A \cdot j_{\text{appl}}/V \cdot (j_{\text{lim,COD}} + j_{\text{lim,Cl}})$  ( $\text{m}^{-1}$ ) as follows,

$$k = 5.2 \times 10^{-6} \frac{A \cdot j_{\text{appl}}}{V(j_{\text{lim,COD}} + j_{\text{lim,Cl}})} \quad (10)$$

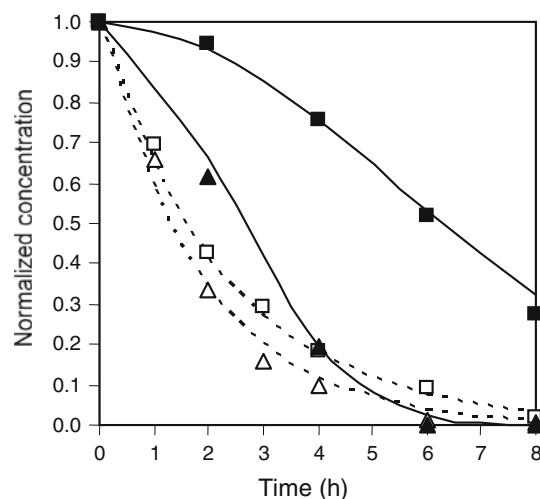
where  $j_{\text{lim,Cl}} = 1Fk_{\text{m}}[\text{Cl}^-]_0$ . Equation 10 indicates that the higher the applied current density with respect to the limiting current density for COD and chloride oxidation, the higher the contribution of the indirect oxidation in the bulk. This implies that, apart from the active chlorine, other oxidants that are electrogenerated participate in the oxidation of COD. It should be kept in mind that the leachate contains a great variety of inorganic ions that can lead to



**Fig. 1** Values of  $k$  parameter given in Table 2 as a function of  $Aj_{\text{appl}}/V(j_{\text{lim,COD}} + j_{\text{lim,Cl}})$



**Fig. 2** Values of  $k'$  parameter given in Table 2 as a function of  $Aj_{\text{appl}}/V(j_{\text{lim,COD}})$



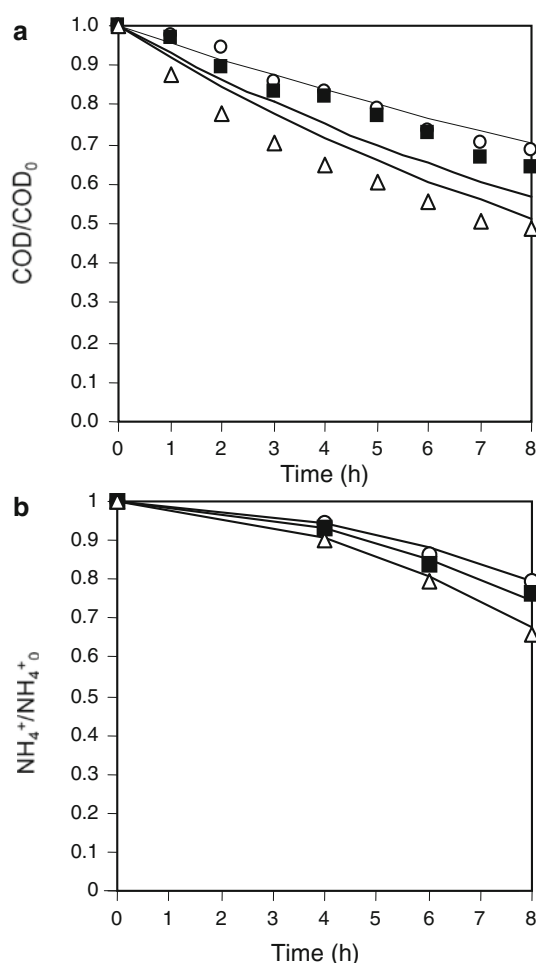
**Fig. 3** Normalized COD (empty symbols) and  $\text{NH}_4^+$  (filled symbols) concentration profiles during the electrochemical treatment of landfill leachates using BDD anodes. Rectangles represent data of Exp. 5 and triangles of Exp. 6. Experimental conditions are given in Table 2. Solid lines represent the simulated  $\text{NH}_4^+$  profile by Eqs. 8, 11 and 12 while dotted lines stand for simulated COD profile predicted by Eqs. 5 and 10. Data presented in our previous work [7]

the formation of strong oxidants. For instance, sulfate ions may be oxidized to peroxodisulfate ions which have been observed to enhance the oxidation of organic matter.

### 3.5 Parameter $k'$

Values of  $k'$  ( $\text{h}^{-2}$ ) were obtained for the different operating conditions used in Exps. 1–17 (Table 2). The slopes of the logarithm of  $[\text{NH}_4^+]_t/[\text{NH}_4^+]_0$  versus the square of the electrolysis time (Eq. 8) were calculated. The values of the slope ( $k'$ ) are given in Table 2. Correlations coefficients higher than 0.972 were obtained. In addition to the  $A/V$  ratio and current density (Eq. 8), ammonium oxidation has been





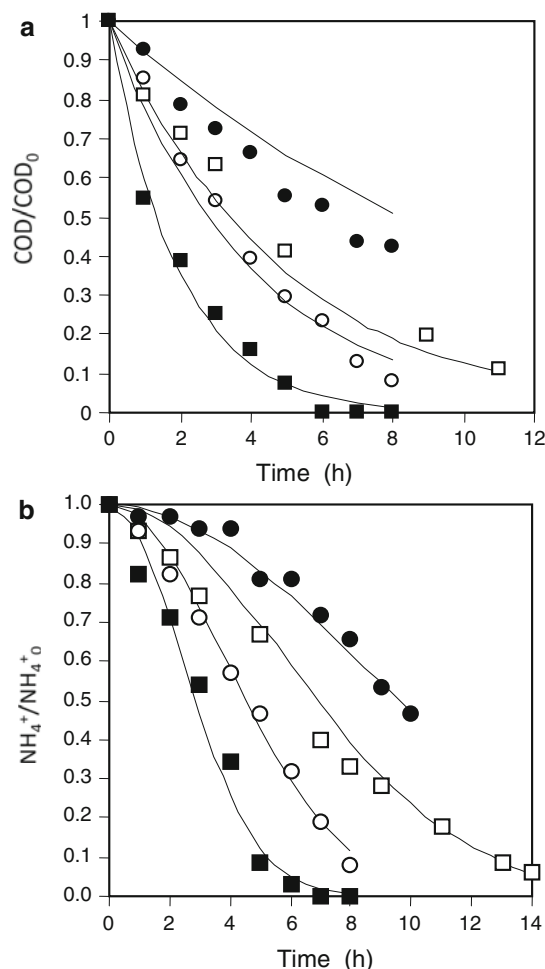
**Fig. 4** Evolution of the normalized concentration of **a** COD and **b** ammonium during the electro-oxidation of landfill leachate obtained in Exps. 1 (open circle), 2 (filled square), and 3 (open triangle), operation conditions given in Table 2. In **a** the results are compared with the profiles predicted by Eq. 1 (Exp. 1) and Eqs. 5 and 10 (Exps. 2 and 3). In **b** the results are compared with simulated data predicted by Eqs. 8 and 11. Data presented in our previous work [12]

found to depend on the concentration of COD [12]. For this reason,  $k'$  was plotted (Fig. 2) as a function of these variables with the initial COD concentration expressed as  $j_{\text{lim,COD}}$ . It was observed that  $k'$  always depended linearly on  $A \cdot j_{\text{appl}} / (j_{\text{lim,COD}} \cdot V)$ . However, for values of  $A \cdot j_{\text{appl}} / (j_{\text{lim,COD}} \cdot V)$  higher than approximately  $9 \text{ m}^{-1}$ , the degree of dependency of  $k'$  on the  $A \cdot j_{\text{appl}} / (j_{\text{lim,COD}} \cdot V)$  increases as indicated by an increase in the slope,

$$\frac{A j_{\text{appl}}}{V j_{\text{lim,COD}}} < 9 \text{ m}^{-1}, \quad k' = 0.0019 \frac{A j_{\text{appl}}}{V j_{\text{lim,COD}}} + 0.0011 \quad (11)$$

$$\frac{A j_{\text{appl}}}{V j_{\text{lim,COD}}} > 9 \text{ m}^{-1}, \quad k' = 0.0102 \frac{A j_{\text{appl}}}{V j_{\text{lim,COD}}} - 0.0662 \quad (12)$$

A representative view of the COD and ammonium concentration profiles obtained with the proposed model and



**Fig. 5** Normalized COD and  $\text{NH}_4^+$  concentration profiles obtained at pilot plant scale in Exps. 18 (filled circle), Exp. 19 (open circle), and Exp. 21 (filled square), and at laboratory scale, Exp. 11 (open square). Solid lines represent simulated data obtained by Eqs. 1, 5, and 10 (COD) and Eqs. 8, 11 and 12 ( $\text{NH}_4^+$ ). Data presented in our previous work [15]

parameters are plotted in Figs. 3, 4, 5 together with the experimental results. Simulated profiles are represented by the solid lines. Overall, good agreement between the experimental and modeling results was obtained.

#### 4 Conclusions

The electro-oxidation using BDD anodes of COD and ammonium contained in leachates generated in municipal landfill sites was modeled considering first-order kinetics for COD oxidation and second-order kinetics for ammonium removal (first order with respect to the concentration of ammonium and first order with respect to the concentration of active chlorine). Direct and hydroxyl radical mediated oxidation close to the anode surface along with indirect oxidation in the bulk solution was considered

responsible for the oxidation of COD. In the description of the model, two operating regimes were defined depending on the value of the limiting current density for the initial COD and  $\text{NH}_4^+$  concentration. For  $j_{\text{lim,COD}} < j_{\text{appl}} \leq (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$ , only direct and  $\cdot\text{OH}$  mediated oxidation reactions close to the anode surface occurred, and the process was mass transfer controlled. The only parameter that needed to be known to predict the behavior of the system was the mass transfer coefficient. For  $j_{\text{appl}} > (j_{\text{lim,COD}} + j_{\text{lim,NH}_4^+})$ , indirect oxidation in the bulk took place which was quantified by an adjustable parameter, defined as a function of  $j_{\text{appl}}/(j_{\text{lim,COD}} + j_{\text{lim,Cl}})$ . Conversely, ammonium oxidation occurred by means of electrogenerated chlorine for which a second adjustable parameter  $k'$  was defined and correlated to the initial COD concentration and the applied current, expressed as  $(A/V) \cdot (j_{\text{appl}}/j_{\text{lim,COD}})$ . The robustness of these models was corroborated by their good description of the experimental results obtained with leachates obtained at different geographical areas, and with variable degrees of pretreatment, therefore with a wide range of compositions and for different operating conditions. The model developed from laboratory scale data was validated at pilot scale with a total anodic area of  $1.05 \text{ m}^2$ . The only re-adjustment required accounted for the change of the hydrodynamic conditions within the electrolytic cell due to differences in the interelectrode gap. For that purpose, the mass transfer coefficient was satisfactorily described by means of conventional generalized dimensionless correlations.

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